

**Final Report**

## **Continuous Polymerization in Miniemulsions**

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**A UNIT OF THE UNIVERSITY SYSTEM OF GEORGIA**

**SCHOOL OF CHEMICAL ENGINEERING**

**ATLANTA, GEORGIA 30332**



**FINAL PROJECT REPORT**  
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| 1. Institution and Address<br>Georgia Tech Research Corp.<br>Georgia Institute of Technology<br>Atlanta, GA 30332-0420 | 2. NSF Program<br>Chem. Biochem & Thermal  | 3. NSF Award Number<br>CBT 8419914     |
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**PART II-SUMMARY OF COMPLETED PROJECT (FOR PUBLIC USE)**

Miniemulsion polymerization is differentiated from classical emulsion polymerization by the fact that the monomer droplets are substantially smaller than found in a classic emulsion and can therefore compete effectively with micelles in the nucleation of polymer particles. To achieve the droplet sizes necessary, high shear is used in conjunction with surfactants and cosurfactants. The mechanism of miniemulsion polymerization is different from that of emulsion polymerization because of the role of the droplets as potential polymer particles. In this work, continuous polymerization in the emulsion and miniemulsion systems have been studied and compared experimentally.

Experimental polymerizations in a CSTR have shown that, at low residence times, the classic emulsions oscillate in conversion whereas the miniemulsions do not. The conversion oscillations in classic emulsion polymerization are due to the alternating presence and absence of micelles in the reaction mixture. In the miniemulsions, the lack of oscillations clearly points to the reduced role of micelles. Further, the miniemulsions achieved a polymerization rate twice that of the classic emulsions. The particle size and conversion data indicate that more particles are present in the miniemulsions. The molecular weight data point to a significant degree of radical segregation in both systems.

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| c. Data on Scientific Collaborators                                             | X                                                    |          |                      |                                       |              |
| d. Information on Inventions                                                    | X                                                    |          |                      |                                       |              |
| e. Technical Description of Project and Results                                 |                                                      |          |                      |                                       |              |
| f. Other (specify)                                                              |                                                      |          |                      |                                       |              |
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## I. INTRODUCTION

Miniemulsion polymerization is a term used to describe heterogeneous polymerization in those systems in which monomer droplets are substantially smaller than found in a typical conventional emulsion polymerization. These polymerizations exhibit some characteristics of the more familiar suspension and emulsion polymerization systems. In each type of polymerization, monomer droplets are dispersed in a continuous aqueous phase in which the monomer is insoluble or only slightly soluble. Surfactants and other colloidal stabilizers are used to stabilize the droplets and prevent particle agglomeration.

While both suspension and emulsion polymerizations are free-radical reactions, each proceeds by a unique mechanism. Initiators for free radical suspension reactions are oil-soluble. The monomer droplets are approximately 1 mm in diameter and each behaves as a small batch reactor, with the monomer reacting to produce polymer. Since the number of free radicals per particle is quite high, the kinetics are those of a bulk free radical polymerization.

Emulsion polymerization, on the other hand, is heavily dependent upon interaction among the various phases. The initial emulsification leads to the formation of a stable emulsion containing 10  $\mu\text{m}$  monomer droplets and surfactant micelles about 0.01  $\mu\text{m}$  in diameter. These micelles are formed from excess surfactant in the continuous phase and have a small amount of monomer at their cores.

Because of their relative size and number, the total surface area of micelles is much greater than the total surface area of the droplets. Thus, free radicals generated by the decomposition of the water-soluble initiator enter micelles much more frequently, resulting in nucleation primarily from micelles. The primary locus of polymerization is the polymer particles thus

formed. As the micelles are nucleated and become polymer particles, monomer molecules diffuse from the monomer droplets, through the continuous phase, and into the polymer particles to supply the polymerization reaction. In the simplest view (Smith-Ewart Case II), termination occurs when a second radical enters the particle. Note that it is possible for the polymerization reaction in any particle to start and stop many times due to absorption of free radicals. The particles eventually grow to a size of about 0.10  $\mu\text{m}$ , forming a final product, referred to as a latex, which is a stable dispersion of polymer particles in the continuous aqueous phase.

In miniemulsion polymerization, high shear is used in combination with surfactants and cosurfactants to produce a fine emulsion of monomer droplets. The monomer droplets are substantially smaller than those found in a typical emulsion polymerization. Reduction of the monomer droplet diameter causes a corresponding increase in the total droplet surface area. This has the effect of making the monomer droplets competitive with the micelles for radical capture since radical absorption is assumed to be competitive on the basis of relative surface area. Also, a reduction in the total number of micelles will occur because the increased surface area of the droplets requires additional surfactant molecules for stabilization purposes.

Given the above considerations, the question arises as to the nature of the kinetics of miniemulsion polymerization. The overall reaction mechanism is thought to contain elements of both the suspension and emulsion mechanisms. However, the extent to which one is prevalent over the other is not known. For example, when using a water-soluble initiator, the relative surface area of droplets to micelles may be such that significant nucleation in the droplets can occur in addition to normal micellar nucleation. This research will address these issues as well as the effects of droplet

nucleation on the well-known oscillatory transients in continuous emulsion polymerization. These questions have been investigated via the bench-scale, continuous miniemulsion polymerization of methyl methacrylate (MMA) with a water-soluble initiator (ammonium persulfate). Comparisons are made between the miniemulsion and conventional continuous emulsion polymerization of MMA in terms of reaction kinetics, particle sizes, and polymer molecular weights.

## II. BACKGROUND

### Cosurfactant Characterization

As discussed above, the small monomer droplet diameters needed to carry out a miniemulsion polymerization are achieved by a combination of high shear, surfactants, and cosurfactants. A good deal of work has been done to identify the best cosurfactants and to quantify the stabilization effects of the cosurfactants. The stability of monomer droplets can be divided into two areas, shear stability and diffusional stability. Shear stability is a measure of the droplets' ability to resist coalescence in the presence of shear forces. Diffusional stability refers to the droplets' ability to resist degradation via diffusion to the continuous phase or other droplets.

Jansson (1) demonstrated that small droplets are diffusionally unstable in the presence of larger droplets. Lack et. al. (2) examined the interfacial aspects of miniemulsion stability and concluded that the overall droplet stability is not comprised solely of diffusional stability. Liquid crystals forming at the oil-water interface apparently increase the droplets' shear stability.

Choi et al. (3,4) and Ugelstad et. al. (5) studied various cosurfactants, recipes and methods of preparation. Cosurfactants are usually water-insoluble, monomer soluble and operate on the principle of eliminating the thermodynamic driving force for diffusion of monomer out of the small



droplets. The studies of Choi and Ugelstad indicate that long chain hydrocarbons and alcohols are favored as cosurfactants. Further, the order of mixing appears to be an important factor in the stability of the miniemulsion. For example, use of a long-chain alcohol dictates that the alcohol, water, and surfactant be thoroughly mixed prior to the addition of the monomer. If, however, sufficient shear is applied, the order of mixing becomes unimportant.

El-Aasser (6) has reported on the formation and stability of miniemulsions. The process of forming a miniemulsion is dependent upon the efficiency of obtaining the initial distribution of monomer droplets and on the effectiveness of maintaining the distribution during the reaction. The most important factors in meeting these criteria are the ratio between the surfactant and cosurfactant and the means by which these substances are mixed together. In addition, the chain length of the hydrocarbon cosurfactant plays a role. Longer-chain molecules tend to increase the long-term stability of the miniemulsion latex.

#### Batch Miniemulsion Polymerizations

Several authors (4,7,8) have studied the use of water-soluble initiators in batch miniemulsion polymerizations of styrene. In these studies, it was reported the bimodal polymer particle size distributions were obtained for various surfactant-cosurfactant ratios. The large particles were about the same size as the initial droplets and were attributed to droplet nucleation. The small particles that were observed were thought to arise from aqueous-phase nucleation phenomena.

The availability of kinetic data for batch miniemulsion polymerization reactions is limited. In an early work, Ugelstad and Hansen (7) reported changes in reaction kinetics for various droplet sizes. They reported

reaction kinetics varying from bulk, to Smith-Ewart Case III and then to Case II kinetics as the droplet size is reduced.

Gilbert et al. (9) have also studied the kinetics of the batch miniemulsion polymerization reaction. Shifts between aqueous phase nucleation and droplet nucleation were observed for various recipes and processing conditions. Their kinetic data show a rate of polymerization that is lower for the case of droplet nucleation. This fact is attributed to a reduced rate of radical entry into the particles.

Both Gilbert (9) and Choi (10) have attempted to define models that describes the polymerization reaction that is taking place. Their models are similar to the Smith-Ewart description of emulsion polymerization. They postulate four kinetic regions. In Region i, monomer droplets are nucleated to become polymer particles. This region is marked by an increasing rate of polymerization as the population of nucleated droplets rises. Region ii is marked by a constant rate of polymerization and appears to have many of the characteristics of Smith-Ewart Case II, including constant monomer concentration at the reaction sites and a constant average number of free radicals per particle. Region iii begins when all of the monomer droplets have been nucleated. In Region iii, the polymerization rate falls due to the consumption of monomer and subsequent drop in the monomer concentration at the reaction sites. Region iv is marked by the onset of the gel effect and continues as the remaining monomer is consumed.

In each of the batch miniemulsion studies discussed above, the monomer used was styrene. In this work, the monomer used will be MMA. Several important differences exist between these monomers. First, MMA is more water-soluble than styrene. Thus, the importance of aqueous-phase nucleation should be more pronounced in the miniemulsion polymerization of MMA. Also, MMA

exhibits a much stronger gel effect than styrene. This fact means that the gel effect may start at lower conversions in MMA polymerizations and could greatly affect the observed kinetics of the reaction taking place in the droplets. Also, note that a continuous reactor system will be used in this work. This reactor configuration permits analysis of reaction kinetics under steady-state rather than dynamic operating conditions.

### III. EXPERIMENTAL APPROACH

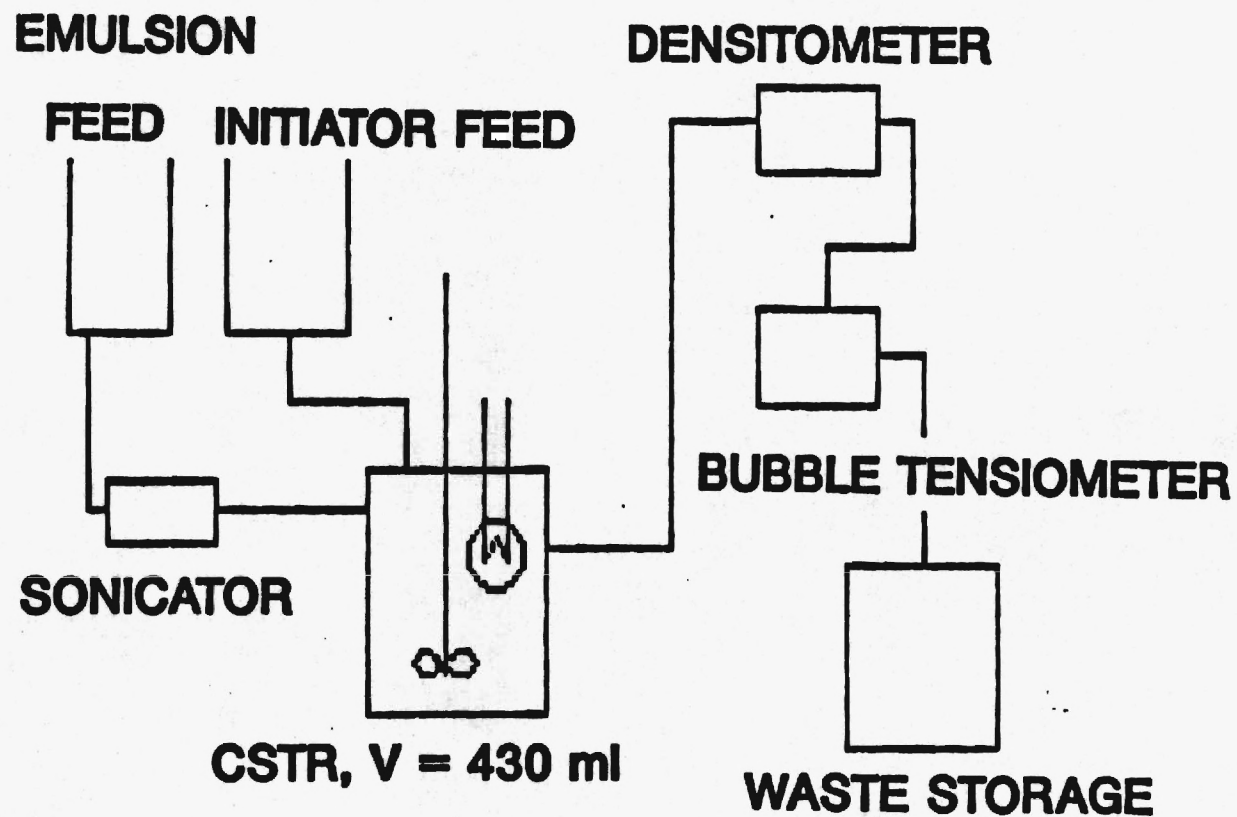
As discussed above, this work involves the use of a continuous reactor system to study the miniemulsion polymerization of MMA. The equipment and experimental procedures used to generate the data are described below.

#### Equipment

A schematic of the experimental system used in this work is shown in Figure 1. The reactor is a two-piece, glass resin kettle with a reaction volume of 430 ml and is operated as a CSTR. Closed-loop control of reactor temperature is achieved by manipulating the temperature of water flowing through a stainless steel coil placed inside the reactor. Other equipment in the reactor includes a two-blade turbine agitator to maintain a constant level of agitation in the reactor and a nitrogen purge which maintains an oxygen-free environment inside the reactor.

Shear is applied to the miniemulsion feed mixture by the sonicator. This device, a Sonic Dismembrator (Model 300) manufactured by Fisher Scientific, consists of a control unit, the sonicator tip, and a continuous flow chamber. The shear field generated by the sonicator within the flow chamber causes, in the presence of a cosurfactant, the reduction of droplet diameter necessary to form a miniemulsion. The maximum power output of the sonicator tip is 300 Watts. The flow chamber clamps over the sonicator tip by means of

Figure 1 Flowsheet of Experimental Apparatus.





an O-ring. The residence time of material inside the flow chamber is small (less than 0.5 min) since its volume is less than 5 ml. Tap water is fed through a jacket on the flow chamber to remove heat generated by the action of the sonicator tip.

Upon exiting from the reactor, the polymer latex is pumped to two on-line analysis instruments. The first of the is an Anton Paar densitometer and provides a means for measuring monomer conversion as described by Schork (11). The unit consists of a flow cell (Model DPR Ye 402) and a serial computer interface (Model DPR-S). The flow cell has a thermostatted U-shaped tube through which the miniemulsion mixture flows. The tube in the cell is excited electronically. As the density of fluid in the tube changes, the frequency of vibration also changes. The relationship between the instrument output,  $\tau$  (proportional to the period of oscillation) and sample density is given by

$$\rho = A [\tau^2 - b] \quad (1)$$

A two-point calibration, using water and air for example, can be performed to determine the constants A and b. The value of  $\tau$  and the cell temperature are displayed on the computer interface.

As a mixture is polymerized, it undergoes an increase in density. The degree of conversion of monomer to polymer is given by (11)

$$x = \frac{v_0 - v_x}{v_0 - v_{100}} \quad (2)$$

The quantity  $v_x$  is calculated from the densitometer data as

$$v_x = \frac{1}{\rho_x} \quad (3)$$

Expressions for  $v_0$  and  $v_{100}$  are defined as

$$v_0 = \frac{V_{H_2O} + V_{MMA} + \frac{NPS}{1.37}}{V_{H_2O} \rho_{H_2O} + V_{MMA} \rho_{MMA} + NPS} \quad (4)$$

$$v_{100} = \frac{V_{H_2O} + V_{pMMA} + \frac{NPS}{1.37}}{V_{H_2O} \rho_{H_2O} + V_{pMMA} \rho_{pMMA} + NPS} \quad (5)$$

Note that these quantities must be calculated for the specific recipe that is used. The term NPS represents non-polymer solids in the recipe, and includes initiator, buffer, surfactant, and any cosurfactant.

The 1.37 factor appearing in equations (4) and (5) is the non-polymer solids density factor. Initially treated as an adjustable parameter, the present value of the factor, 1.37, has been found to give conversion measurements from the densitometer that are accurate to within one percent for a number of polymerizations.

The other on-line analysis instrument used in this work is the surface tensiometer or bubble tensiometer. The theory of this device is given by Schork (12). The unit consists of a jacketed flow cell, a pressure transducer, a signal filter, and a digital display meter. The mixture being analyzed is fed into the bottom of the flow cell. A side arm allows material to drain from the cell and maintains constant cell volume at about 20 ml. Two tubes are immersed just under the liquid surface in the cell. The immersed tip of one tube is very large while the immersed tip of the other is very small. Nitrogen gas is fed through the tubes at low pressure causing bubbles to be formed at the tips. The back pressure of the bubble formation in each tube varies with surface tension, more so in the case of the small tip. Side arms on each tube are connected to opposite ports of a differential pressure transducer (Sentra Systems Model 239) which measures this pressure difference. The pressure transducer generates a voltage signal which is

passed through a low-pass filter (Frequency Devices 744/745 Series), which extracts the DC component of the wave-form. The filtered signal is displayed on a digital volt meter. By manipulating the zero and span, the digital volt meter can be made to display the value of surface tension directly, in dyne/cm. The filtered signal may be sent to a strip-chart recorder or a digital data acquisition system. Surface tension measurements with this device are accurate to within 2 to 5 percent.

#### Procedures

The basic chemical recipe used in this work is shown in Table I. The MMA monomer, supplied by Rohm and Haas and inhibited with 25 ppm hydroquinone (HDQ) was purified by vacuum distillation at 35°C and 65 mmHg vacuum. The surfactant used was BDH Chemicals Specially Pure sodium lauryl sulfate (SLS). The remaining chemicals were Fisher A.C.S. certified reagent grade. Note that only the miniemulsion experiments included the cosurfactant. Hexadecane was chosen because it was desired to have a liquid cosurfactant at ambient temperature.

The emulsion feed mixture was prepared by mixing the monomer, water, buffer, and cosurfactant, if any. The mixture was sparged with nitrogen for 30 minutes and then emulsified for 30 minutes with a high-speed agitator after the surfactant was added. After the initial sparging, a nitrogen blanket was maintained in the emulsion tank. The initiator feed mixture was prepared while the sparging of the emulsion tank was taking place. The contents of the initiator tank were sparged with nitrogen for the duration of the experiment.

The emulsion feed mixture was then pumped to the reactor. As it was being filled, the contents of the reactor were raised to the reaction temperature of 40°C. When the reactor was filled to capacity with the emulsion feed, the flow of the initiator mixture to the reactor was started.

Table I

Basic Miniemulsion Recipe

| <u>Monomer</u>                             | <u>Mass, g</u> | <u>Vol., ml</u> | $\frac{\text{mol}}{2\text{H}_2\text{O}}$ | <u>PPHM</u><br>(parts per hundred<br>(monomer)) |
|--------------------------------------------|----------------|-----------------|------------------------------------------|-------------------------------------------------|
| Methyl-methacrylate<br>(MMA)               | 2378           | 2530            | ---                                      | 100                                             |
| <u>Emulsion</u>                            |                |                 |                                          |                                                 |
| H <sub>2</sub> O                           | 3620           | 3620            | ---                                      | 152.2                                           |
| Sodium Lauryl Sulfate<br>(SLS)             | 15.46          | ---             | .010                                     | .65                                             |
| Hexadecane<br>(C16)                        | 47.56          | ---             | .039                                     | 2.00                                            |
| Sodium bicarbonate<br>(SBC)                | 4.50           | ---             | .010                                     | .19                                             |
| <u>Initiator</u>                           |                |                 |                                          |                                                 |
| H <sub>2</sub> O                           | 1740           | 1740            | ---                                      | 73.2                                            |
| Ammonium Persulfate<br>(A <sub>m</sub> Ps) | 12.23          | ---             | .010                                     | .51                                             |



This action constituted the start of the reaction. Shortly after the reaction start, the pump which delivered the polymer latex to the analysis instruments was activated.

#### IV. RESULTS

Two different series of experiments were performed. In the first, the effects of reactor residence time on reaction kinetics in the emulsion and miniemulsion systems were studied. In the second series of experiments, the effects of varying the molar monomer-to-water ratio at fixed residence time were investigated.

##### Reactor Residence Time Studies

The conversion-versus-time profiles for an emulsion and a miniemulsion at residence time of 25 minutes are shown in Figure 2. The oscillatory behavior of the emulsion profile has been explained by Omi et al. (13). Initially, there is a burst of particles formed as micelles are nucleated to become polymer particles. As the conversion rises, the particles grow in size and require increasingly larger amounts of surfactant to stabilize the particle surface area. Thus, the population of micelles is eventually driven to zero and no new particles can form. At this point, the conversion is a maximum. The polymer particles continue to grow but are slowly washed out of the reactor. This action causes the conversion to decrease toward a minimum while the surfactant concentration increases. At the point of minimum conversion, micelles can again be present, meaning that a new generation of particles can be formed. Thus, the cycle can be repeated either as sustained or damped oscillations. Similar arguments can be made if homogeneous, rather than micellar nucleation is thought to be dominant. In the miniemulsion, the lack

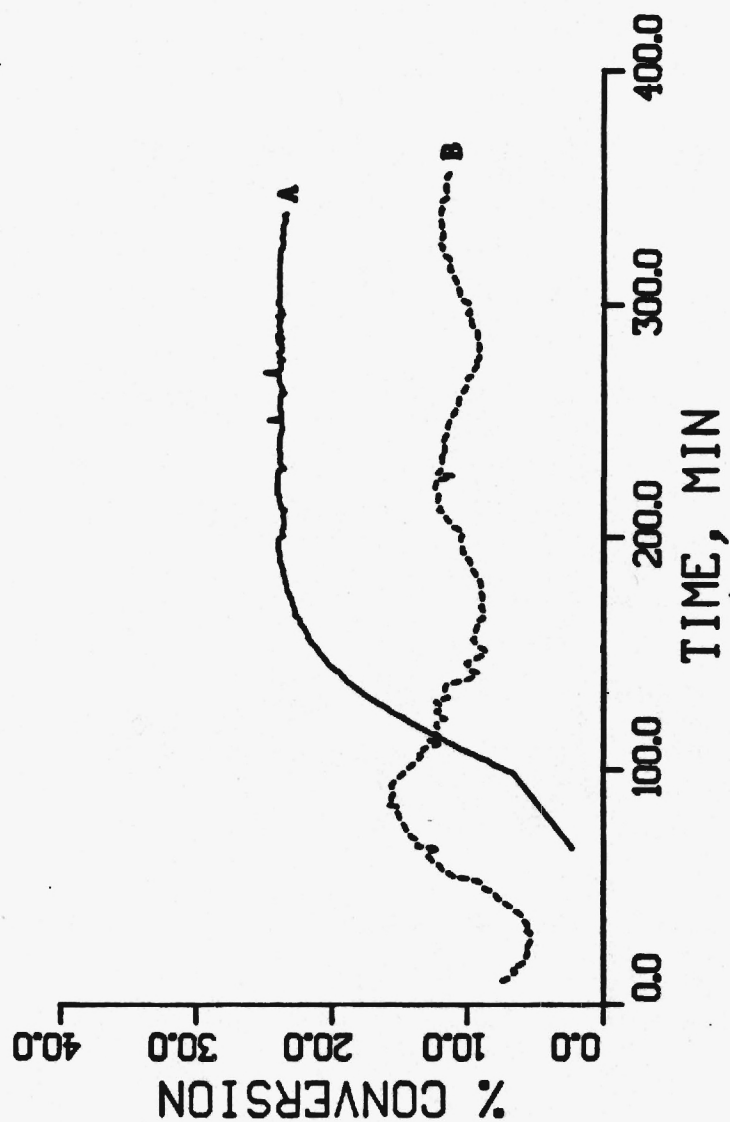


Figure 2 Comparison of Conversion-versus-Time Profiles for Miniemulsion, (A) and Conventional Emulsion, (B).

of oscillation points to the greatly diminished role of micellar or homogeneous nucleation.

Figures 3, 4, and 5 present other data obtained for the experiments shown in Figure 2. The surface tension profiles, Figure 3, show a higher surface tension and a decreased tendency to oscillate for the miniemulsion than for the conventional emulsion. Since surface tension is a measure of free surfactant concentration, it provides a direct indication of the relative saturation of the aqueous phase. In the case of the conventional emulsion, the oscillations reflect the alternating periods of particle nucleation and particle growth and washout. The higher surface tension in the miniemulsion reflects the increased droplet surface area and subsequent decrease in free surfactant.

The molecular weight data, Figure 4, show little difference between the two systems. The fact that such high molecular weights were attained suggested a significant degree of radical segregation exists in both polymerization systems. The absence of a small molecular weight peak in the miniemulsion distribution indicate the absence of any suspension-like (bulk) polymerization kinetics. Thus, if any droplets were nucleated, they exhibited the same radical segregation behavior as the nucleated micelles.

The particle size distributions (by transmission electron microscopy) for the respective product latexes are shown in Figure 5. The particle size distribution of the miniemulsion product has a higher mean and is somewhat broader than its conventional emulsion counterpart. The broader distribution in the miniemulsion suggests a shear-induced particle formation mechanism compatible with droplet nucleation.

The steady-state conversion data for a number of conventional and miniemulsion polymerizations using the recipe in Table I are summarized in

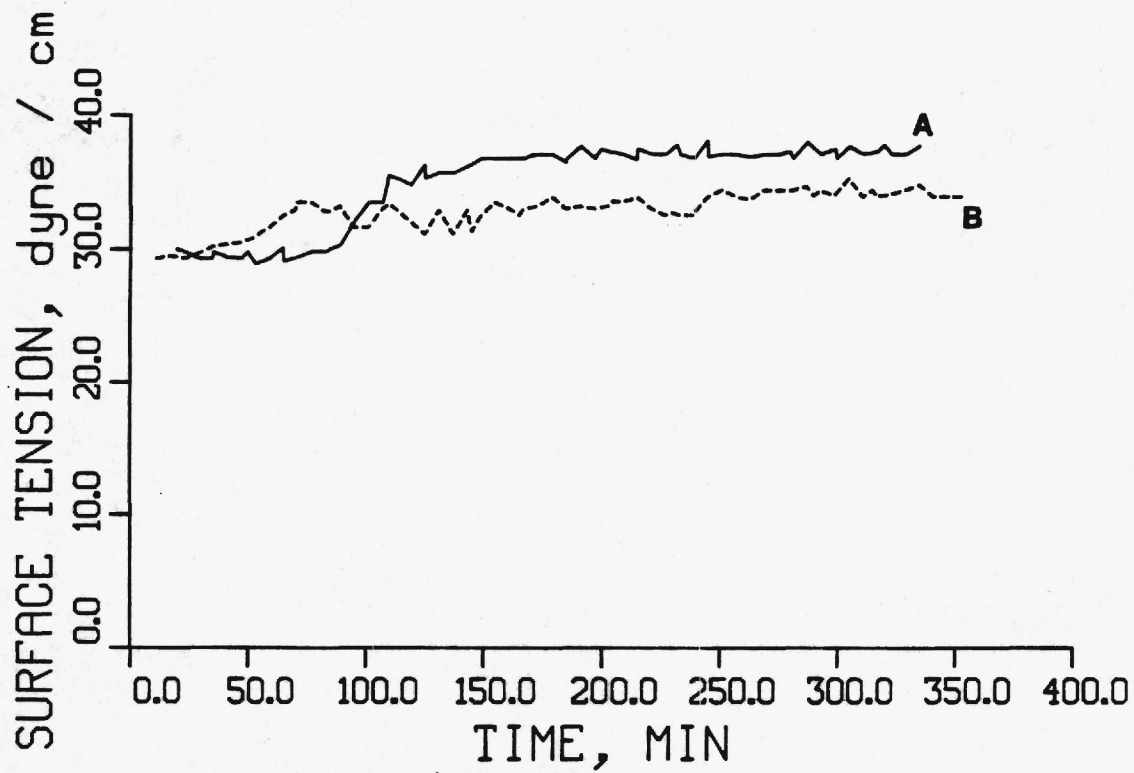


Figure 3 Surface Tension-versus-Time Profiles for Miniemulsion, (A) and Conventional Emulsion, (B).



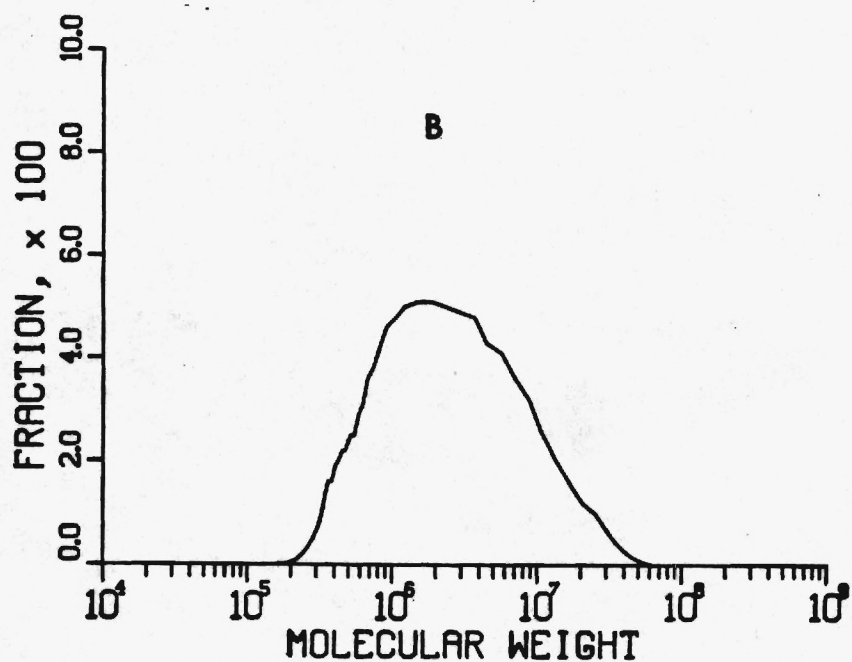
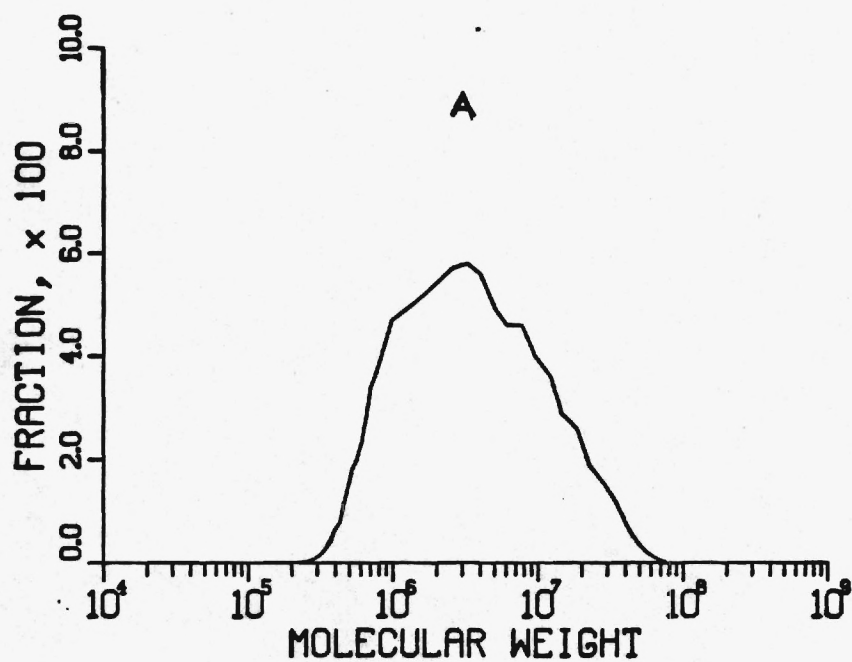


Figure 4 Molecular Weight Distributions for Polymer Samples from Miniemulsion, (A) and Classic Emulsion, (B).

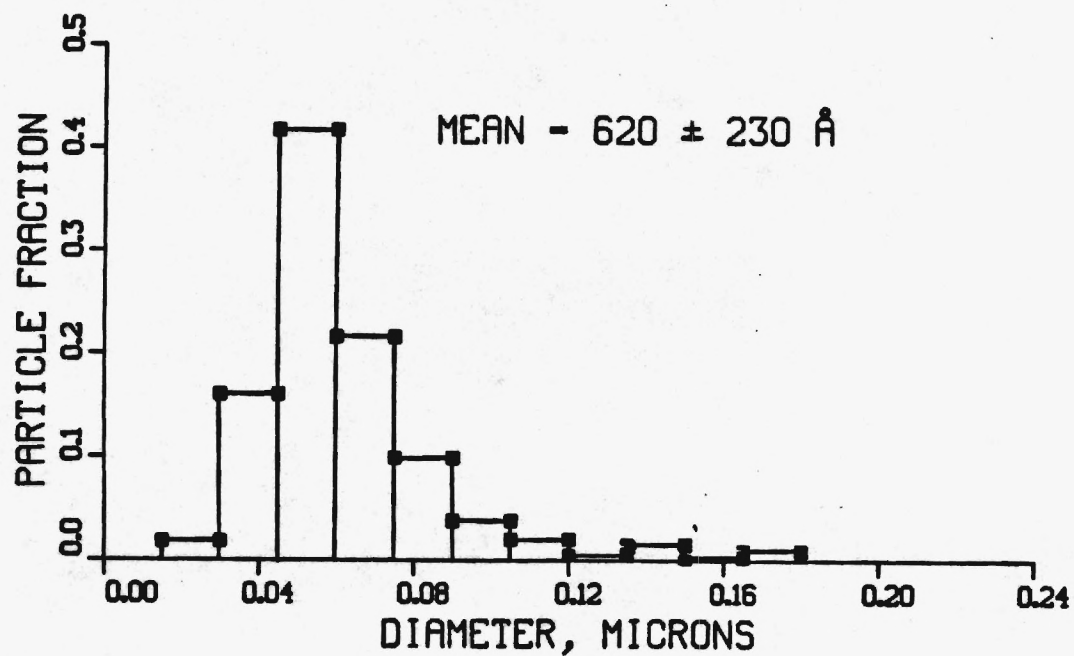
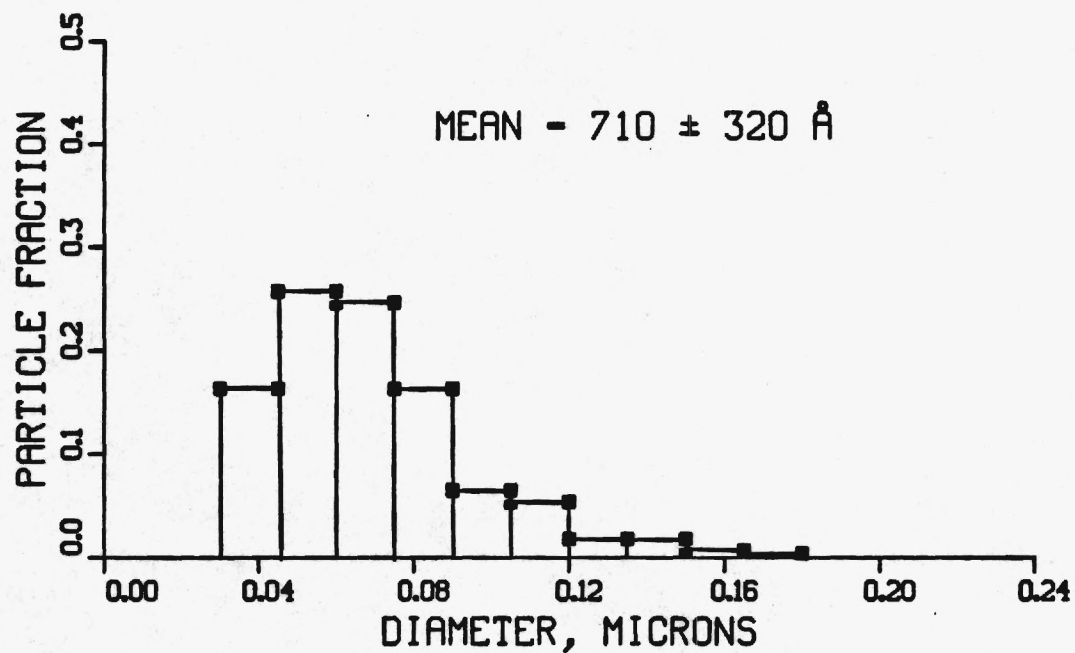


Figure 5 Particle Size Distributions for Polymer Samples from Miniemulsion, (A) and Conventional Emulsion, (B).

Figure 6. For the oscillatory conventional emulsion polymerizations, the steady-state conversion was estimated as the average of the maxima and minima of the oscillations. At high residence times, no difference between the two reaction systems is observed. This is due to the fact that the gel effect predominates at high conversion, thus obscuring any observable particle nucleation phenomena. At low residence times, the conventional emulsion runs oscillated in conversion while the miniemulsions achieved higher conversion levels and exhibited no oscillations in conversion.

The various data shown in Figures 2 through 5 lead to several conclusions concerning miniemulsion polymerization as carried out in this work. The conversion and surface tension profiles indicate that the role of the micelles has been greatly diminished in the miniemulsion system. However, the lack of any significant differences in the molecular weight and particle size distributions would seem to indicate that either micellar nucleation is the dominant mechanism of particle formation or that the nucleated droplets are small enough to exhibit a significant degree of radical segregation.

#### Effect of Monomer-to-Water Ratio

Additional polymerization were carried out to study of the effects of lowering the monomer-to-water ratio in both conventional emulsion and miniemulsion polymerizations. By decreasing the total amount of monomer in the reaction mixture, a reduction in the total number of monomer droplets was to be achieved. If the droplets serve as the primary reaction locus, the reaction rate is expected to fall as the number of droplets in the reaction mixture is reduced. The recipes for lower monomer to water ratio were developed by reducing the monomer in the recipe then scaling the entire recipe to get the desired volume. In the case of the conventional emulsions, the recipes were designed to give the same total number of micelles as the emulsion recipe

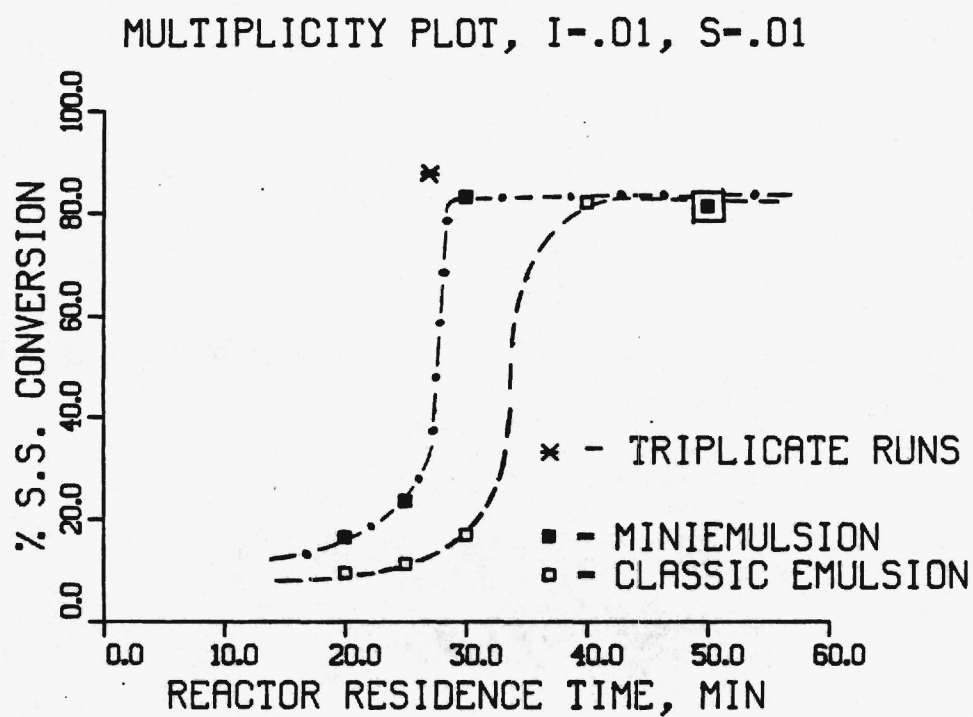


Figure 6 Multiplicity Plot Showing Steady State Conversion Levels for Miniemulsion and Classic Emulsion as a Function of Reactor Residence Time.

listed in Table I. Note that the recipe listed in Table I was used as a basis for these reduced monomer experiments and that a reactor residence time of 25 minutes was chosen. Comparisons between the various reduced monomer recipes were made by calculating the volumetric steady-state reaction rates and then plotting the rates as a function of the molar monomer-to-water ratio.

An expression for the reaction rate is given by Equation (6).

$$R_p = \frac{X_F M_{MMA}}{V T_R} \quad (6)$$

Note that the reaction volume can be expressed either as the total volume of the reactor or as the aqueous fraction of the total reactor volume. The latter method is appropriate for particle nucleation occurring in the aqueous phase and is representative of conventional emulsion polymerization. The former method reflects changes in the number of particles per unit volume of reaction mixture and is appropriate to a system involving nucleation in monomer droplets.

The reaction rate data for a series of conventional emulsions and mini-emulsions at various reduced monomer levels are summarized in Figures 7 and 8. In Figure 7, the rate is expressed as a function of the total reaction volume while in Figure 8 the rate is calculated on the basis of the aqueous fraction of the reaction volume. In Figure 8, the conventional emulsion data show a decreasing rate of polymerization as the molar monomer-to-water ratio is decreased. As noted above, these emulsion polymerization experiments were designed to produce the same total number of micelles as the recipe listed in Table I. As will be shown, the aqueous-phase concentration of micelles decreased due to the change in water content of the recipes. This concentration decrease is in spite of the fact that the total number of micelles actually increased slightly as the monomer-water ratio was reduced. The polymeriza-



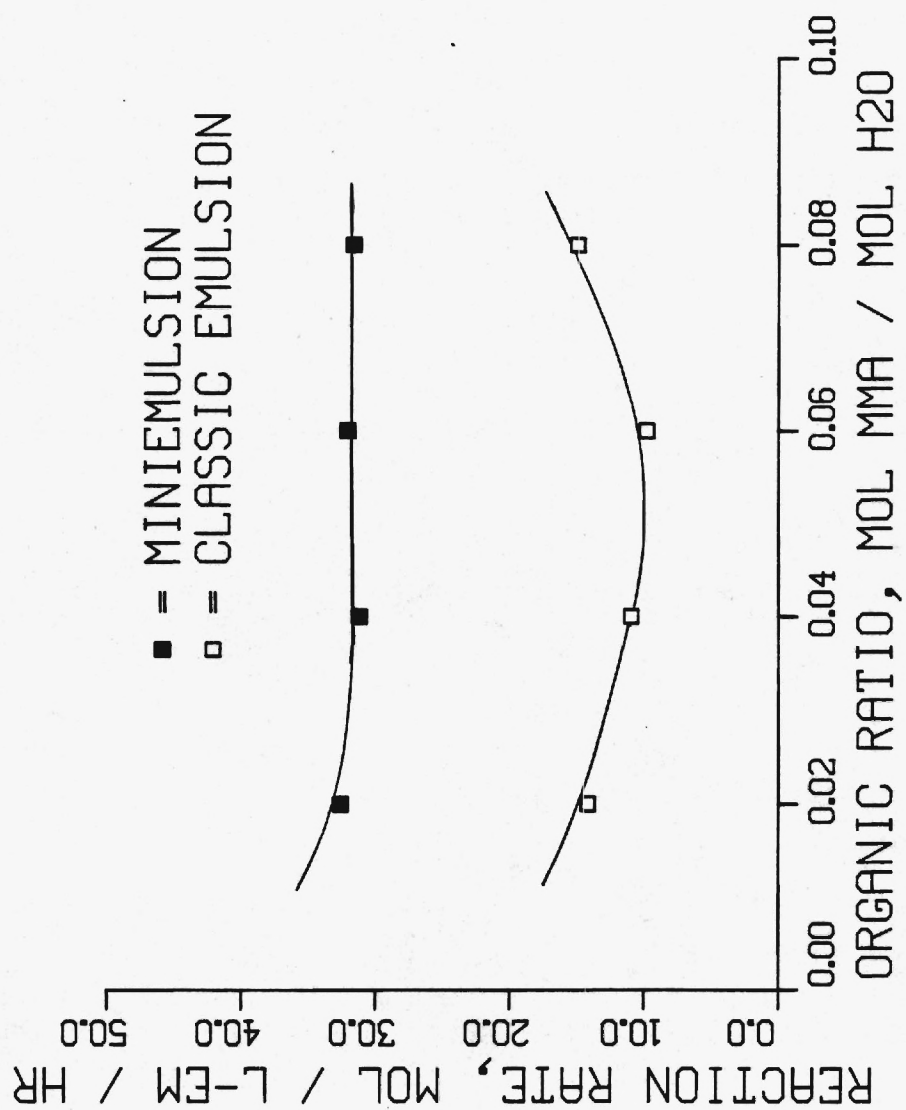


Figure 7 Reaction Rate versus Molar Monomer-to-Water Ratio where Rate is on the Basis of Total Reaction Volume.

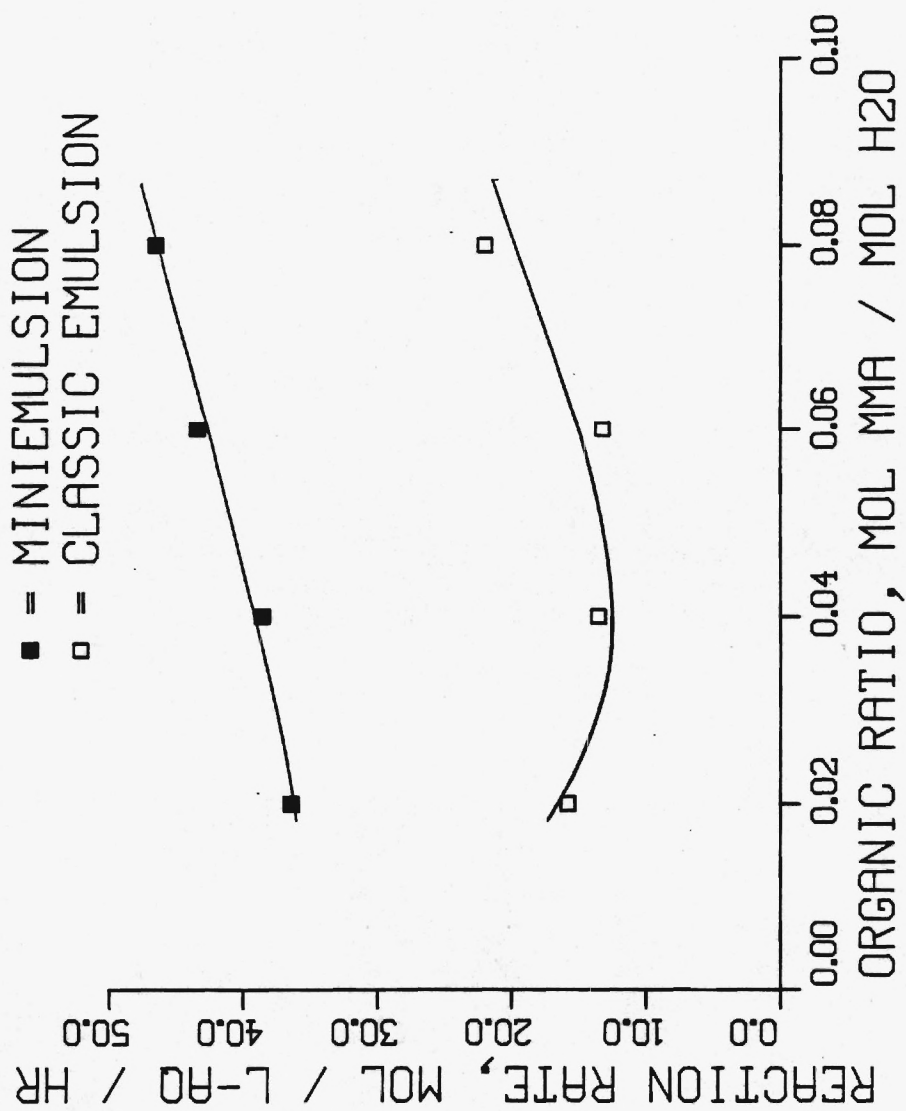


Figure 8 Reaction Rate versus Molar Monomer-to-Water Ratio where Rate is on the Basis of Aqueous Reaction Volume.

tion rate in conventional emulsion system has been shown to be proportional to the number of polymer particles. Since micellar nucleation in the aqueous phase is assumed to be the primary mechanism of particle formation, a decreasing rate implies a decrease in the number of micelles per unit volume of aqueous phase. As indicated above, these conventional emulsion recipes show a drop in the number of micelles and, hence, the number of particles, thus producing a subsequent decline in the polymerization rate. At a monomer to water ratio of 0.02 the rate of polymerization rises again. This is due to the early onset of the gel effect at low monomer levels.

The reaction rate data for the miniemulsion polymerizations show strikingly different behavior. In Figure 7, the rate is shown to be essentially constant with decrease in the monomer-to-water ratio. These observations imply that the number of particles, and hence the number of droplets remain constant with respect to the total volume of the reaction mixture. The large difference in the reaction rates between the conventional emulsion and miniemulsion systems make it clear that the mechanism of polymerization is different in the miniemulsion system.

To investigate the essentially constant rate of polymerization for the miniemulsions (Figure 8), calculations were made to determine the number of monomer droplets and micelles for the recipes used in these runs. Assuming a value of 0.57 g SLS/  $\text{g H}_2\text{O}$ , the fractional saturation of the available droplet surface area was determined for a miniemulsion with a molar monomer-to-water ratio of 0.08 in which spherical droplets of diameter 0.2  $\mu\text{m}$  were assumed. The droplet diameter was chosen on the basis of measurements made on the unpolymerized miniemulsion with the Malvern Autosizer IIc. Using the assumed CMC and the fractional saturation determined above, the number and diameter of monomer droplets were calculated for miniemulsions with monomer-water ratios of 0.06, 0.04 and 0.02. The results of this calculation

are summarized in Table II. The fractional saturation was found to be 0.17. This result indicates that the cosurfactant provides a large measure of stability to the droplets. For monomer-to-water ratios of 0.08, 0.06, and 0.04, these calculations indicate a constant number of monomer droplets (potential polymer particles). This is due to fortuitious adjustments in the surfactant concentration for various values of monomer-to-water ratio. A rise in the number of droplets for a monomer-to-water ratio in Table II is reflected in a slightly higher rate of polymerization in Figure 7. A range of values for the CMC have been reported in the literature and range from 0.15 to 2.0 g per %  $H_2O$ . The value used here is well within this range. The interpretation of the rate data is, however, dependent on the value of CMC used.

Using the CMC value determined above, (0.57 g / %  $H_2O$ ), the concentration of micelles for each of the conventional emulsion polymerization recipes was calculated. Ten micron spherical droplets and complete coverage of the droplet surface area by surfactant were assumed. Table III lists the results of these calculations. The conclusion drawn from Figure 8 that a decrease in the aqueous phase concentration of micelles occurred as the monomer-water ratio was reduced is verified by the data shown in Table III. The high rate of reaction at a monomer-to-water ratio of 0.02 (Figure 8) is not in agreement with these calculations and is attributable to the early onset of the gel effect at low monomer loading.

Another feature of the data presented in Figures 7 and 8 that must be explained is the difference in the polymerization rates for the two systems. As can be seen, the rate for the miniemulsion system is about twice the rate of the conventional emulsion system. This result is in direct opposition to the reported results of Gilbert (9), Ugelstad (8), and Choi (10). Ugelstad

Table II

Summary of CMC and Droplet Diameter  
Calculations for Miniemulsion Recipes

| $\frac{o}{w}, \frac{\text{mol MMA}}{\text{mol H}_2\text{O}}$ | $N_{D-em}^1$          | $N_{D-aq}^2$          | $D, \mu m$ |
|--------------------------------------------------------------|-----------------------|-----------------------|------------|
| .08                                                          | $7.66 \times 10^{16}$ | $1.13 \times 10^{17}$ | .200       |
| .06                                                          | $7.48 \times 10^{16}$ | $1.01 \times 10^{17}$ | .188       |
| .04                                                          | $7.65 \times 10^{16}$ | $0.95 \times 10^{17}$ | .168       |
| .02                                                          | $9.71 \times 10^{16}$ | $1.08 \times 10^{17}$ | .127       |

1 - number of droplets per liter miniemulsion mixture

2 - number of droplets per liter of aqueous fraction of miniemulsion mixture

$$CMC = 0.57 \frac{g \text{ SLS}}{l \text{ H}_2\text{O}}$$



Table III

Summary of Calculation of Number of  
Micelles for Conventional Emulsion Recipes

| $\frac{o}{w} \frac{\text{mol MMA}}{\text{mol H}_2\text{O}}$ | $N_{m - em}^1$        | $N_{m - aq}^2$        |
|-------------------------------------------------------------|-----------------------|-----------------------|
| .08                                                         | $4.69 \times 10^{19}$ | $6.90 \times 10^{19}$ |
| .06                                                         | $4.77 \times 10^{19}$ | $6.45 \times 10^{19}$ |
| .04                                                         | $4.87 \times 10^{19}$ | $6.02 \times 10^{19}$ |
| .02                                                         | $5.01 \times 10^{19}$ | $5.60 \times 10^{19}$ |

1 - number of micelles per liter emulsion mixture

2 - number of micelles per liter of aqueous fraction of emulsion mixture

$$CMC = 0.57 \frac{\text{g SLS}}{\text{l H}_2\text{O}}$$

(7), however, has reported rates of polymerization for styrene-hexadecane miniemulsions exposed to high shear rates which are substantially higher than those of the equivalent conventional emulsions. One possible explanation lies in the number of polymer particles being generated in the two systems. To achieve the faster rate, polymerization in the miniemulsion system would have to generate more particles than the conventional emulsion system. Calculations to verify this can be made using the particle size distribution and conversion data for the runs shown in Figure 2. Table IV summarizes the results of these calculations assuming all particles are spherical and have a diameter equal to the mean of the distribution. As can be seen, approximately twice as many particles are generated in the miniemulsion as in the conventional emulsion. Recall that the molecular weight data (Figure 4) implied similar polymerization kinetics within the particles in both systems. Based on the particle number calculations shown in Table IV, the reaction rates per particle for the miniemulsion and conventional emulsion are  $7.71 \times 10^{-17}$  mol/hr/particle and  $7.07 \times 10^{-17}$  mol/hr/particle respectively. Therefore, the molecular weight, particle size and reaction rate data show that, while a different mechanism of particle formation exists in the miniemulsion system, the mechanism of polymerization after particle formation is similar to that occurring in the conventional emulsion system.

## V. DISCUSSION

The various experiments that have been performed have demonstrated a number of interesting points. First, the conventional emulsion polymerizations were seen to oscillate in conversion whereas the miniemulsions did not. This observation indicates that the role of micelles in the miniemulsion reaction has been greatly reduced. In the experiments in which the monomer-water

Table IV

Calculation of Number of Polymer Particles  
for Conventional Emulsion and Miniemulsion Systems

| <u>RXN</u> | <u>Type</u>  | <u>SS Conv, %</u> | <u>PSD Mean, Å</u> | <u>N<sub>p</sub>, <sup>particle</sup><br/> &amp; mixture</u> |
|------------|--------------|-------------------|--------------------|--------------------------------------------------------------|
| 80         | Mini         | 23.9              | 710                | $4.09 \times 10^{17}$                                        |
| 8P         | Conventional | 11.2              | 620                | $2.09 \times 10^{17}$                                        |

ratio was varied, the mechanism of particle formation in the conventional emulsion system appears to be micellar. In the miniemulsion system, the monomer droplets were shown to be the source of polymer particles.

The molecular weight data have shown that a high degree of radical segregation exists in both systems. This fact suggests that the polymer particles in each system polymerize and grow in a similar fashion.

Ugelstad et. al. (7) have reported similar results for batch miniemulsion of polymerizations of styrene in which hexadecane was used as a cosurfactant. Table V summarizes these results. Note that a homogenizer was used to provide the necessary high shear in Ugelstad's work. By varying the intensity of the homogenization, Ugelstad was able to change the droplet size and thus change the free-emulsifier concentration. The free-emulsifier concentration is a measure of the amount of surfactant that is not saturating the surface of the droplets and reflects the droplet size and the concentration of micelles. Thus, small values of the free-emulsifier correspond to small concentrations of micelles. Note the interdependence of conversion, particle number, and free-emulsifier concentration in Table V. Ugelstad's results also show that conversion is directly related to the particle number, as was postulated above for the present work. Thus, the similarity between the experimental results in the present work and Ugelstad's results serve to confirm the polymerizations involving the use of a cosurfactant in the present work were of the miniemulsion type.

The differences and similarities between the conventional emulsion and miniemulsion polymerization systems in the present work can be explained by considering the mechanisms of particle formation and growth in each system. In conventional emulsion polymerization, new polymer particles arise from the nucleation of micelles. However, since surfactant molecules must also

Table V

Experimental Results of Ugelstad

| <u>Experiment</u> | Free-Emulsifier                        | Particle Number,          | <u>Conversion</u> <sup>2</sup> |
|-------------------|----------------------------------------|---------------------------|--------------------------------|
|                   | <u>Concentration, g/dm<sup>3</sup></u> | <u>No./dm<sup>3</sup></u> |                                |
| A                 | 2.01                                   | $1.9 \times 10^{17}$      | 115                            |
| B                 | 1.20                                   | $1.2 \times 10^{16}$      | 20                             |
| C                 | 0.16                                   | $5.4 \times 10^{16}$      | 50                             |
| D                 | 0.14                                   | $7.7 \times 10^{16}$      | 75                             |
| E                 | 0.12                                   | $2.9 \times 10^{17}$      | 190                            |

1 -- No Homogenization

2 -- Estimated monomer conversion, in g/dm<sup>3</sup>, at 100 minutes after reaction start



saturate the surface areas of the monomer droplets and the growing polymer particles, micelles may not always be present in the reactor. During those periods in which micelles are not present, no new particles are formed and those present at the time micelles disappear are eventually washed out of the reactor. In miniemulsion polymerization, on the other hand, the mechanism of particle formation involves the nucleation of monomer droplets. At low to moderate conversion levels, droplets will always be present and thus the nucleation of monomer droplets can keep pace with the washout of existing polymer particles and eliminate the possibility of oscillation. Since it has been shown that polymer particles in both systems exhibit similar radical segregation and thus similar particle growth characteristics, the miniemulsion system is able to maintain a greater number of particles (due to the large number of monomer droplets) and a greater degree of conversion than the conventional emulsion system.

## VI. SUMMARY

Under this great dynamic data for the continuous miniemulsion polymerization of methyl methacrylate have been developed. The data clearly show that the monomer droplets serve as the source of polymer particles in the miniemulsion system. However, due to the extremely small size of the monomer droplets (induced by sonication) the polymer particles in the miniemulsion system exhibit growth characteristics which are similar to those for particles in a conventional continuous emulsion polymerization system.

## NOMENCLATURE

|            |                                                                   |
|------------|-------------------------------------------------------------------|
| $A$        | = densitometer constant, g/ml                                     |
| $b$        | = densitometer constant, dimensionless                            |
| $M_{MMA}$  | = moles of monomer in the recipe, mol                             |
| $NPS$      | = non-polymer solids; includes initiator, buffer cosurfactant, g  |
| $R_p$      | = reaction rate, mol/l/hr                                         |
| $T_R$      | = reactor residence time, hr                                      |
| $V$        | = reactor volume, l                                               |
| $V_{H_2O}$ | = volume of water in recipe, ml                                   |
| $V_{MMA}$  | = volume of monomer in recipe, ml                                 |
| $X_F$      | = fractional conversion of monomer at steady state, dimensionless |
| $x$        | = fractional conversion of monomer to polymer, dimensionless      |

### Greek Symbols

|           |                                                                  |
|-----------|------------------------------------------------------------------|
| $v_x$     | = specific volume at $x$ fractional conversion, ml/g             |
| $v_0$     | = specific volume at 0 % conversion, ml/g                        |
| $v_{100}$ | = specific volume at 100 % conversion, ml/g                      |
| $\rho$    | = density, g/ml                                                  |
| $\rho_x$  | = density of polymer solution at $x$ fractional conversion, g/ml |
| $\tau$    | = densitometer output, dimensionless                             |

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## PUBLICATIONS AND PRESENTATIONS

### RESULTING FROM THIS WORK

#### PUBLICATIONS

Chen, C. M., L. Gothjelpsen, and F. J. Schork, "Computer Simulation of Continuous Miniemulsion Polymerization," Polymer Process Eng., 4 (1) (1986).

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Barnette, D. T., and F. J. Schork, "Continuous Miniemulsion Polymerization," AIChE Annual Meeting, Miami Beach, November, 1986.

CONTINUOUS MINIEMULSION POLYMERIZATION

A THESIS

Presented to

The Faculty of the Division of Graduate Students

By

Darrell Thomas Barnette

In Partial Fulfillment

of the Requirements for the Degree

Doctor of Philosophy in Chemical Engineering

Georgia Institute of Technology

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## SUMMARY

Miniemulsion polymerization is differentiated from classical emulsion polymerization by the fact that the monomer droplets are substantially smaller than found in a classic emulsion and can therefore compete effectively with micelles in the nucleation of polymer particles. To achieve the droplet sizes necessary, high shear is used in conjunction with surfactants and cosurfactants. The term cosurfactant is standard terminology in this field and refers to organic additives which are not surface active but which enhance the stabilization properties of the surfactant. The mechanism of miniemulsion polymerization is different from that of emulsion polymerization because of the role of the droplets as potential polymer particles. In this work, continuous polymerization in the emulsion and miniemulsion systems have been studied and compared both experimentally and through computer simulation.

Conclusions from previous studies concerning the importance of the cosurfactant to obtaining stable distributions of small monomer droplets have been confirmed. Experimental polymerizations in a CSTR have shown that, at low residence times, the classic emulsions oscillate in conversion whereas the miniemulsions do not. The conversion oscillations in classic emulsion polymerization are due to the alternating presence and absence of micelles in the reaction mixture. In the miniemulsions, the lack of oscillations clearly points to the reduced role of micelles. Further, the miniemulsions achieved a polymerization rate twice that of the classic emulsions. The particle size and conversion

data indicate that more particles are present in the miniemulsions. The molecular weight data point to a significant degree of radical segregation in both systems.

Other experimental data show that the polymerization rate in the miniemulsion system is a function of the concentration of monomer droplets in the emulsion. In the classic emulsion system, the polymerization rate is a function of the concentration of micelles. The source of particle formation in the two systems is different. In the miniemulsion system, the monomer droplets are the primary source of polymer particles while micelles are the main source of polymer particles in the classic emulsion system.

Mathematical models have been developed which describe the classic emulsion and miniemulsion systems. The models are based upon a series of differential material balances and are solved numerically. While predictions of the dynamic behavior of the systems are beyond the scope of these models, good agreement between simulation and experimental results have been obtained at steady state reactor conditions. In addition, it is also shown that the models predict more polymer particles in the minimeulsion system than in the classic emulsion, as was observed in the experiments.